

WHAT IS CLAIMED AS NEW AND IS DESIRED TO BE SECURED BY LETTERS  
PATENT OF THE UNITED STATES IS:

1. A process of atom or group transfer radical  
polymerization, comprising the steps of:

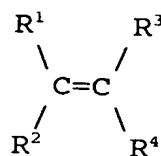
5 polymerizing one or more radically polymerizable  
monomers in the presence of an initiator having a radically  
transferable atom or group, a transition metal compound and a  
ligand to form a (co)polymer, the transition metal compound  
being capable of participating in a redox cycle with the  
10 initiator and a dormant polymer chain, and the ligand being  
any N-, O-, P- or S- containing compound which can coordinate  
in a  $\sigma$ -bond to the transition metal or any carbon-containing  
compound which can coordinate in a  $\pi$ -bond to the transition  
metal, such that direct bonds between the transition metal and  
15 growing polymer radicals are not formed, and  
isolating the formed (co)polymer.

2. The process of Claim 1, wherein the amounts of said  
monomer(s), said initiator, said transition metal compound and  
said ligand are such that growing radicals are present during  
20 said polymerizing in a concentration in the range of from  $10^{-9}$   
mol/L to  $10^{-6}$  mol/L, and dormant polymer chains are present  
during said polymerizing in a concentration in the range of  
from  $10^{-4}$  mol/L to 1 mol/L.

3. The process of Claim 2, wherein the concentration of  
25 said growing radicals is from  $10^{-8}$  mol/L to  $10^{-6}$  mol/L.

4. The process of Claim 2, wherein the concentration of said dormant polymer chains is from  $10^{-4}$  mol/L to 1 mol/L.

5. The process of Claim 1, wherein said monomer(s) are of the formula:



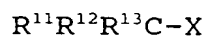
wherein  $\text{R}^1$  and  $\text{R}^2$  are independently selected from the group consisting of H, halogen, CN,  $\text{CF}_3$ , straight or branched alkyl of from 1 to 20 carbon atoms,  $\alpha, \beta$ -unsaturated straight or branched alkenyl or alkynyl of 2 to 10 carbon atoms,  $\alpha, \beta$ -unsaturated straight or branched alkenyl of 2 to 6 carbon atoms substituted with a halogen,  $\text{C}_3\text{-C}_8$  cycloalkyl, heterocyclyl,  $\text{C}(=\text{Y})\text{R}^5$ ,  $\text{C}(=\text{Y})\text{NR}^6\text{R}^7$  and  $\text{YC}(=\text{Y})\text{R}^8$ ; where Y may be  $\text{NR}^8$  or O;  $\text{R}^5$  is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy;  $\text{R}^6$  and  $\text{R}^7$  are independently H or alkyl of from 1 to 20 carbon atoms, or  $\text{R}^6$  and  $\text{R}^7$  may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring; and  $\text{R}^8$  is H, straight or branched  $\text{C}_1\text{-C}_{20}$  alkyl or aryl; and

$\text{R}^3$  and  $\text{R}^4$  are independently selected from the group consisting of H, halogen,  $\text{C}_1\text{-C}_6$  alkyl and  $\text{COOR}^9$ , where  $\text{R}^9$  is H, an alkali metal, or a  $\text{C}_1\text{-C}_6$  alkyl group; or

R<sup>1</sup> and R<sup>3</sup> may be joined to form a group of the formula (CH<sub>2</sub>)<sub>n'</sub> or a group of the formula C(=O)-Y-C(=O), where n' is from 2 to 6, the group (CH<sub>2</sub>)<sub>n'</sub> may be substituted with from 1 to 2n' halogen atoms or C<sub>1</sub>-C<sub>4</sub> alkyl groups, and Y is as defined above; and

at least two of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are H or halogen.

6. The process of Claim 1, wherein said initiators is of the formula:



where:

X is selected from the group consisting of Cl, Br, I, OR<sup>10</sup>, SR<sup>14</sup>, SeR<sup>14</sup>, OP(=O)R<sup>14</sup>, OP(=O)(OR<sup>14</sup>)<sub>2</sub>, OP(=O)OR<sup>14</sup>, O-N(R<sup>14</sup>)<sub>2</sub> and S-C(=S)N(R<sup>14</sup>)<sub>2</sub>, where R<sup>10</sup> is alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R<sup>14</sup> is aryl or a straight or branched C<sub>1</sub>-C<sub>20</sub> alkyl group, and where an N(R<sup>14</sup>)<sub>2</sub> group is present, the two R<sup>14</sup> groups may be joined to form a 5- or 6-membered heterocyclic ring; and

R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> are each independently selected from the group consisting of H, halogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>8</sub> cycloalkyl, C(=Y)R<sup>5</sup>, C(=Y)NR<sup>6</sup>R<sup>7</sup>, COCl, OH, CN, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkyñyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C<sub>1</sub>-C<sub>6</sub> alkyl in which from 1 to all of the hydrogen atoms are

replaced with halogen and C<sub>1</sub>-C<sub>6</sub> alkyl substituted with from 1 to 3 substituents selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkoxy, aryl, heterocyclyl, C(=Y)R<sup>5</sup>, C(=Y)NR<sup>6</sup>R<sup>7</sup>, oxiranyl and glycidyl;

5           where R<sup>5</sup> is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and R<sup>6</sup> and R<sup>7</sup> are independently H or alkyl of from 1 to 20 carbon atoms, or R<sup>6</sup> and R<sup>7</sup> may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus  
10       forming a 3- to 6-membered ring;  
such that no more than two of R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> are H.

7. The process of Claim 6, wherein no more than one of R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> is H.

8. The process of Claim 1, wherein said transition metal  
15       compound is of the formula M<sub>t</sub><sup>n+</sup>X'<sub>n</sub>, where:

M<sub>t</sub><sup>n+</sup> may be selected from the group consisting of Cu<sup>1+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Eu<sup>2+</sup>, Ru<sup>3+</sup>, Cr<sup>2+</sup>, Cr<sup>3+</sup>, Mo<sup>2+</sup>, Mo<sup>3+</sup>, W<sup>2+</sup>, W<sup>3+</sup>, Mn<sup>3+</sup>, Mn<sup>4+</sup>, Rh<sup>3+</sup>, Rh<sup>4+</sup>, Re<sup>2+</sup>, Re<sup>3+</sup>, Co<sup>+</sup>, Co<sup>2+</sup>, V<sup>2+</sup>, V<sup>3+</sup>, Zn<sup>+</sup>, Zn<sup>2+</sup>, Au<sup>+</sup>, Au<sup>2+</sup>, Ag<sup>+</sup> and Ag<sup>2+</sup>;

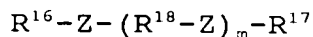
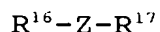
20       X' is selected from the group consisting of halogen, C<sub>1</sub>-C<sub>6</sub>-alkoxy, (SO<sub>4</sub>)<sub>1/2</sub>, (PO<sub>4</sub>)<sub>1/3</sub>, (R<sup>14</sup>PO<sub>4</sub>)<sub>1/2</sub>, (R<sup>14</sup><sub>2</sub>PO<sub>4</sub>), triflate, hexafluorophosphate, methanesulfonate, arylsulfonate, CN and R<sup>15</sup>CO<sub>2</sub>, where R<sup>15</sup> is H or a straight or branched C<sub>1</sub>-C<sub>6</sub> alkyl

group which may be substituted from 1 to 5 times with a halogen; and

$n$  is the formal charge on the metal ( $0 \leq n \leq 7$ ).

9. The process of Claim 1, wherein said ligand is selected from the group consisting of:

compounds of the formulas:



where:

$R^{16}$  and  $R^{17}$  are independently selected from the group consisting of H,  $C_1-C_{20}$  alkyl, aryl, heterocyclyl and  $C_1-C_6$  alkyl substituted with  $C_1-C_6$  alkoxy,  $C_1-C_4$  dialkylamino,  $C(=Y)R^5$ ,  $C(=Y)R^6R^7$  and  $YC(=Y)R^8$ , where Y may be  $NR^8$  or O;  $R^5$  is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy;  $R^6$  and  $R^7$  are independently H or alkyl of from 1 to 20 carbon atoms, or  $R^6$  and  $R^7$  may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring; and  $R^8$  is H, straight or branched  $C_1-C_{20}$  alkyl or aryl;

Z is O, S,  $NR^{19}$  or  $PR^{19}$ , where  $R^{19}$  is selected from the same group as  $R^{16}$  and  $R^{17}$ , and where Z is  $PR^{19}$ ,  $R^{19}$  can also be  $C_1-C_{20}$ -alkoxy;

each  $R^{18}$  is independently a divalent group selected from the group consisting of  $C_3-C_8$  cycloalkanediyl,  $C_3-C_8$

cycloalkenediyl, arenediyl and heterocyclylene where the covalent bonds to each Z are at vicinal positions, and C<sub>2</sub>-C<sub>4</sub> alkylene and C<sub>2</sub>-C<sub>4</sub> alkenylene where the covalent bonds to each Z are at vicinal positions or at  $\beta$ -positions; and

5 m is from 1 to 6;

compounds of the above formulas where R<sup>16</sup> and R<sup>17</sup> can be joined to form a saturated, unsaturated or heterocyclic ring;

10 compounds of the above formulas where each of R<sup>16</sup>-Z and R<sup>17</sup>-Z form a ring with the R<sup>18</sup> group to which the Z is bound to form a linked or fused heterocyclic ring system;

compounds of the above formulas where one or both of R<sup>16</sup> and R<sup>17</sup> are heterocyclyl, and in which Z is a covalent bond, CH<sub>2</sub> or a 4- to 7-membered ring fused to R<sup>16</sup> or R<sup>17</sup> or both;

CO;

15 porphyrins and porphycenes, which may be substituted with from 1 to 6 halogen atoms, C<sub>1</sub>-C<sub>6</sub> alkyl groups, C<sub>1</sub>-C<sub>6</sub>-alkoxy groups, C<sub>1</sub>-C<sub>6</sub> alkoxycarbonyl, aryl groups, heterocyclyl groups, and C<sub>1</sub>-C<sub>6</sub> alkyl groups further substituted with from 1 to 3 halogens;

20 compounds of the formula R<sup>20</sup>R<sup>21</sup>C(C(=Y)R<sup>5</sup>)<sub>2</sub>, where Y and R<sup>5</sup> are as defined above, and each of R<sup>20</sup> and R<sup>21</sup> is independently selected from the group consisting of H, halogen, C<sub>1</sub>-C<sub>20</sub> alkyl, aryl and heterocyclyl, and R<sup>20</sup> and R<sup>21</sup> may be joined to form a C<sub>3</sub>-C<sub>6</sub> cycloalkyl ring or a hydrogenated aromatic or  
25 heterocyclic ring, any of which (except for H and halogen) may be further substituted with 1 to 5 C<sub>1</sub>-C<sub>6</sub> alkyl groups, C<sub>1</sub>-C<sub>6</sub>

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alkoxy groups, halogen atoms, aryl groups, or combinations thereof; and

arenes and cyclopentadienyl ligands, where said cyclopentadienyl ligand may be substituted with from one to five methyl groups, or may be linked through an ethylene or propylene chain to a second cyclopentadienyl ligand.

10. The process of Claim 1, wherein the initiator is present in a concentration of from  $10^{-4}$  M to 1 M.

11. The process of Claim 1, wherein the initiator and monomer(s) are present in amounts providing a molar ratio of from  $10^{-4}$ :1 to  $10^{-1}$ :1 of initiator to monomer(s).

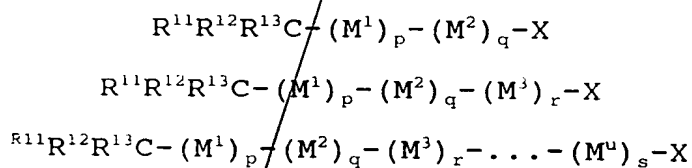
12. The process of Claim 1, wherein the transition metal compound is present in an amount providing a molar ratio of transition metal compound to initiator of from 0.001:1 to 10:1.

13. The process of Claim 1, wherein the ligand is present in an amount providing a ratio of (a) coordination sites on the transition metal compound to (b) coordination sites which the ligand will occupy of from 0.1:1 to 100:1.

14. The process of Claim 1, wherein the monomer, initiator, transition metal compound and ligand are selected

such that (a) the rate of initiation in said polymerizing step is not less than 1,000 times slower than (b) the rate of propagation in said polymerizing step or of transfer of the radically transferable group to the polymer radical.

15. A copolymer of the formula:



wherein X is selected from the group consisting of Cl, Br, I, OR<sup>10</sup>, SR<sup>14</sup>, SeR<sup>14</sup>, O-N(R<sup>14</sup>)<sub>2</sub>, S-C(=S)N(R<sup>14</sup>)<sub>2</sub>, H, OH, N<sub>3</sub>, NH<sub>2</sub>, COOH and CONH<sub>2</sub>, where

R<sup>10</sup> is alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R<sup>14</sup> is aryl or a straight or branched C<sub>1</sub>-C<sub>20</sub> alkyl group, and where an N(R<sup>14</sup>)<sub>2</sub> group is present, the two R<sup>14</sup> groups may be joined to form a 5- or 6-membered heterocyclic ring,

R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> are each independently selected from the group consisting of H, halogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>8</sub> cycloalkyl, C(=Y)R<sup>5</sup>, C(=Y)NR<sup>6</sup>R<sup>7</sup>, COCl, OH, CN, C<sub>2</sub>-C<sub>20</sub> alkenyl, C<sub>2</sub>-C<sub>20</sub> alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C<sub>1</sub>-C<sub>6</sub> alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and C<sub>1</sub>-C<sub>6</sub> alkyl substituted

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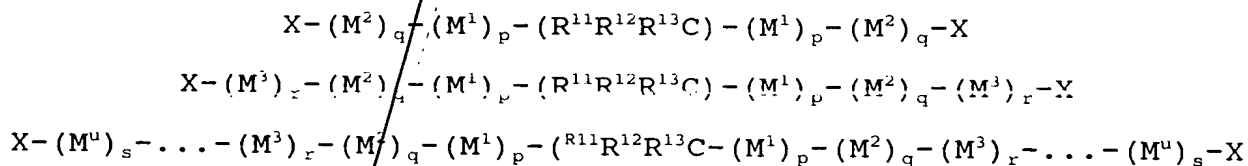
with from 1 to 3 substituents selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkoxy, aryl, heterocyclyl, C(=Y)R<sup>5</sup>, C(=Y)NR<sup>6</sup>R<sup>7</sup>, oxiranyl and glycidyl, where

R<sup>5</sup> is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and R<sup>6</sup> and R<sup>7</sup> are independently H or alkyl of from 1 to 20 carbon atoms, or R<sup>6</sup> and R<sup>7</sup> may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring,

such that no more than two of R<sup>11</sup>, R<sup>12</sup> and R<sup>13</sup> are H, and

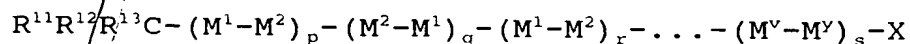
M<sup>1</sup>, M<sup>2</sup>, M<sup>3</sup>,... up to M<sup>u</sup> are each a radically polymerizable monomer selected such that the monomers in adjacent blocks are not identical, and p, q, r,... up to s are independently selected such that the number average molecular weight of each block is from 1,000 to 250,000 g/mol;

the following formulas:

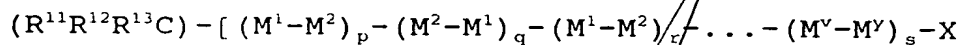


wherein R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup>, X, M<sup>1</sup>, M<sup>2</sup>, M<sup>3</sup>,... up to M<sup>u</sup>, and p, q, r,... up to s are as defined above;

of the formulas:



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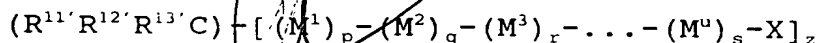
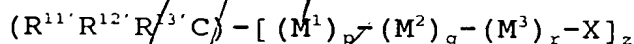
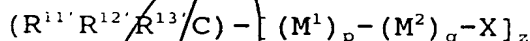
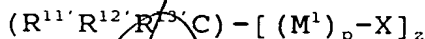


where  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $X$  are as defined above,

$M^1$  and  $M^2$  are different radically-polymerizable monomers, and  $M^v$  is one of  $M^1$  and  $M^2$  and  $M^y$  is the other of  $M^1$  and  $M^2$ , and

$p$ ,  $q$ ,  $r$ , ... up to  $s$  are independently selected such that the number average molecular weight of the copolymer is from 1,000 to 1,000,000 g/mol;

of the formulas:

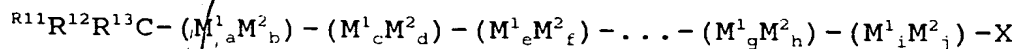


where  $R^{11'}$ ,  $R^{12'}$  and  $R^{13'}$  are the same as  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  with the proviso that  $R^{11'}$ ,  $R^{12'}$  and  $R^{13'}$  combined contain from 2 to 5  $X$  groups, where  $X$  is as defined above;

$M^1$ ,  $M^2$ ,  $M^3$ , ...  $M^u$  are as defined above; and

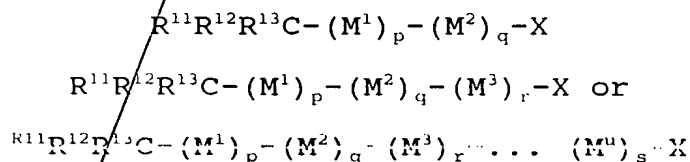
$z$  is from 3 to 6; and

of the formula:



where  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $X$  are as defined above,  $M^1$  and  $M^2$  are different radically-polymerizable monomers, and  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ ,  $f$ , ... up to  $g$  and  $h$  are non-negative numbers independently selected such that  $a + b = c + d = 100$ , and any or all of  $(e + f)$ ,  $(g + h)$  and  $(i + j) = 100$  or 0, wherein the  $a:b$  ratio is from 100:0 to 0:100, the  $c:d$  ratio is from 95:5 to 5:95, such that  $c < a$  and  $d > b$ , and where applicable, the  $e:f$  ratio is from 90:10 to 10:90, such that  $e < c$  and  $f > d$ , and the endpoints of the molar ratio ranges of first monomer to second monomer in successive blocks progressively decrease or increase by 5 such that the  $e:f$  ratio is from 5:95 to 95:5, such that  $e \neq c$  and  $f \neq d$ , and the  $i:j$  ratio is from 0:100 to 100:0, such that  $i \neq e$  and  $j \neq f$ .

16. The copolymer of Claim 15, having a formula:



wherein  $X$  is selected from the group consisting of  $Cl$ ,  $Br$ ,  $I$ ,  $OR^{10}$ ,  $SR^{14}$ ,  $SeR^{14}$ ,  $O-N(R^{14})_2$ ,  $S-C(=S)N(R^{14})_2$ ,  $H$ ,  $OH$ ,  $N_3$ ,  $NH_2$ ,  $COOH$  and  $CONH_2$ ; and where

$R^{10}$  is alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide,  $R^{14}$  is aryl or a straight or branched  $C_1-C_{20}$  alkyl

group, and where an  $N(R^{14})_2$  group is present, the two  $R^{14}$  groups may be joined to form a 5- or 6-membered heterocyclic ring,

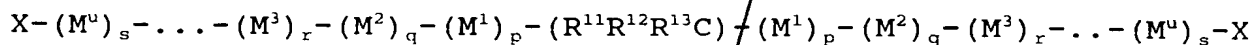
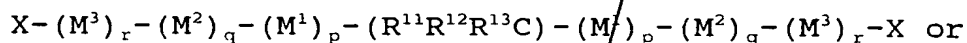
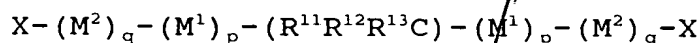
$R^{11}$ ,  $R^{12}$  and  $R^{13}$  are each independently selected from the group consisting of H, halogen,  $C_1-C_{20}$  alkyl,  $C_3-C_8$  cycloalkyl,  $C(=Y)R^5$ ,  $C(=Y)NR^6R^7$ , COCl, OH, CN,  $C_2-C_{20}$  alkenyl,  $C_2-C_{20}$  alkynyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl,  $C_1-C_6$  alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen and  $C_1-C_6$  alkyl substituted with from 1 to 3 substituents selected from the group consisting of  $C_1-C_4$  alkoxy, aryl, heterocyclyl,  $C(=Y)R^5$ ,  $C(=Y)NR^6R^7$ , oxiranyl and glycidyl, where

$R^5$  is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; and  $R^6$  and  $R^7$  are independently H or alkyl of from 1 to 20 carbon atoms, or  $R^6$  and  $R^7$  may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring,

such that no more than two of  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are H, and

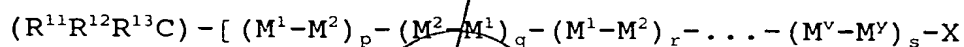
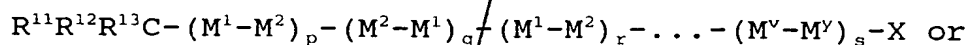
$M^1$ ,  $M^2$ ,  $M^3$ ,.... up to  $M^u$  are each a radically polymerizable monomer selected such that the monomers in adjacent blocks are not identical, and  $p$ ,  $q$ ,  $r$ ,.... up to  $s$  are independently selected such that the number average molecular weight of each block is from 1,000 to 250,000 g/mol.

17. The copolymer of Claim 15, having a formula:



wherein  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $X$ ,  $M^1$ ,  $M^2$ ,  $M^3$ ,... up to  $M^u$ , and  $p$ ,  $q$ ,  $r$ ,... up to  $s$  are as defined in Claim 15.

18. The copolymer of Claim 15, having a formula:

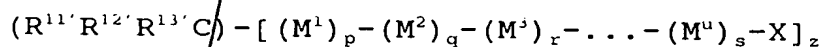
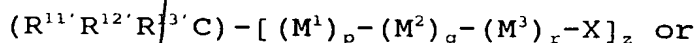
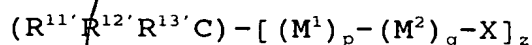
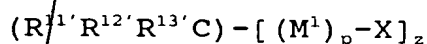


where  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and  $X$  are as defined in Claim 15,

$M^1$  and  $M^2$  are different radically-polymerizable monomers, and  $M^v$  is one of  $M^1$  and  $M^2$  and  $M^v$  is the other of  $M^1$  and  $M^2$ , and

$p$ ,  $q$ ,  $r$ ,... up to  $s$  are independently selected such that the number average molecular weight of the copolymer is from 1,000 to 1,000,000 g/mol.

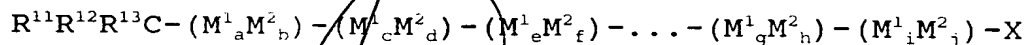
19. The copolymer of Claim 15, having a formula:



where  $R^{11'}$ ,  $R^{12'}$  and  $R^{13'}$  are the same as  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  as defined in Claim 15, with the proviso that  $R^{11'}$ ,  $R^{12'}$  and  $R^{13'}$  combined contain from 2 to 5 X groups, where X is as defined above;

5  $M^1, M^2, M^3, \dots M^u$  are as defined above; and  
z is from 3 to 6.

20. The copolymer of Claim 15, having the formula:



10 where  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$  and X are as defined in Claim 15,  $M^1$  and  $M^2$  are different radically-polymerizable monomers, and a, b, c, d, e, f, ... up to g and h are non-negative numbers independently selected such that  $a + b = c + d = 100$ , and any or all of  $(e + f)$ ,  $(g + h)$  and  $(i + j) = 100$  or 0, wherein the a:b ratio is from 100:0 to 0:100, the c:d ratio is from 95:5 to 5:95, such that  $c < a$  and  $d > b$ , and where applicable, the e:f ratio is from 90:10 to 10:90, such that  $e < c$  and  $f > d$ , and the endpoints of the molar ratio ranges of first monomer to second monomer in successive blocks progressively decrease or increase by 5 such that the e:f ratio is from 5:95 to 95:5, such that  $e \neq c$  and  $f \neq d$ , and the i:j ratio is from 0:100 to 100:0, such that  $i \neq e$  and  $j \neq f$ .

add  
a<sup>1</sup>

add  
b<sup>2</sup>

add  
c<sup>1</sup>  
add c<sup>1</sup>